Published in Anal Chim Acta. 2019;1060:114-24.

Time weighted average concentrations measured with Diffusive Gradients in Thin films (DGT)

Alexandra Altier[a], Martín Jiménez-Piedrahita[a], Ramiro Uribe[b], Carlos Rey-Castro[a], Josep Galceran[a], Jaume Puy[a*]

[a]*Departament de Química. Universitat de Lleida, and AGROTECNIO, Rovira Roure 191, 25198 Lleida, Catalonia, Spain;* [b]*Department of Physics, University of Tolima, 730006 Ibagué, Colombia*

Abstract

Time weighted average (TWA) concentrations can improve the assessment of water quality. DGT (Diffusive Gradients in Thin films) devices have been suggested as simple tools to measure TWA metal concentrations, but the connection of TWA with c_{DGT} has not been rigorously discussed. It is shown here that c_{DGT} is the average DGT-labile concentration along the deployment, which suggests that it is well suited to correlate with toxicity effects. In terms of real species, c_{DGT} is a good estimator of the TWA concentration for simple metal solutions (no ligands are present) when the accumulation takes place under perfect sink conditions. Differences between c_{DGT} and the TWA concentration for short pulses (<40 min), when the transient regime becomes relevant, are reported. In the presence of complexes, c_{DGT} contains the TWA of the product of the labile fraction times the relative diffusivity of the complex (to that of the free metal). This means that c_{DGT} can underestimate the TWA of the total metal concentration due to the presence of complexes less mobile than the free metal or not fully labile. These findings are illustrated with Cd, Ni, Mg or Ni+nitrilotriacetic acid (NTA) solutions. When only one complex is relevant, as in the Ni+NTA system, a simple correction factor can yield the TWA concentration from c_{DGT}.

* Corresponding author, email address: jpuy@quimica.udl.cat, Phone 34 973 702529, Fax 34 973 702924

Keywords: passive sampling, concentration fluctuation, time average concentration, lability degree, transient effects, complexation

Highlights:

- $c^*_{T,M,Av}$ is the time-weighted average of total bulk concentrations
- DGT devices deployed in simple metal solutions yield $c^*_{T,M,Av}$
- Time accumulations bending down lead to c_{DGT} underestimating $c^*_{T,M,Av}$
- c_{DGT} underestimates $c^*_{T,M,Av}$ when partially labile or large complexes are present
- Corrections of c_{DGT} to estimate $c^*_{T,M,Av}$ for a dominant-complex case are reported

1. Introduction

Spatial and temporal variations in pollutant concentrations are common in surface waters, where a wide range of natural and anthropogenic processes affects water quality. Most environmental screening methods for pollutants in water involve grab sampling [1]. Conventional sampling techniques provide only a snapshot of the pollution situation at the sampling instant, so that they may be not representative of the water conditions when concentrations of pollutants fluctuate. Intensive monitoring or the use of automatic stations could mitigate this effect, but it would increase the monitoring costs. Additionally, speciation can be affected by microbial activity, changes in redox conditions, oxygenation or aggregation phenomena during the period from collection to analysis in the laboratory [2, 3].

Passive sampling can be an alternative analytical approach that overcomes some of these limitations [4, 5]. Integrative passive samplers can provide time-weighted average (TWA) concentrations of a wide range of environmental pollutants over the deployment time, rather than a snapshot at one particular moment. They can be deployed in a range of environments, for short (e.g. days) or long term (e.g. months) monitoring, depending on the analyte and the binding capacity of the collector phase. Since pollutants are preconcentrated during the deployment, detection limits and uncertainty of the measurement are improved [6-8].

There are various types of passive samplers with different design characteristics addressed to sample different aquatic pollutants [9-13]. Some of them, like Polar Organic Integrative sampler (POCIS), some kinds of Solid Phase Micro Extraction fibres (SPME) and DGT, are used for integrative measurements [4]. DGT differs from other passive samplers mainly in the incorporation of a diffusive disc (or layer) between the accumulation element (binding phase) and the sample. This key feature reduces the influence of bulk transport phenomena (such as convection) on the accumulation of the analyte and allows the determination of DGT-labile metal concentrations in many environmental systems from the mass of analyte accumulated in the binding layer and its diffusion coefficient across the gel [8, 14-16].

There are a few studies in the literature about the response of DGT devices to changes in concentration during the deployment time. Some of these works deal with metals [6, 17, 18], but others are applied to toxic organic compounds [13, 16, 19, 20], or to nutrients such as inorganic P or N [21-23]. Although most of the concepts here developed can be useful in the measurement of TWA concentrations of most analytes of environmental interest, this work focusses on the case of metals. To the best of our knowledge, none of

the works devoted to metals establishes analytical expressions relating DGT concentrations and average concentrations.

DGT devices were exposed to a pulsed metal concentration to simulate fluctuations. We start discussing results of perfect sink accumulations in solutions with just metal (Cd or Ni). Accumulations of Mg are used to exemplify a system where the accumulation is non-linear with time (i.e. perfect-sink conditions are not reached). Short pulses that prevent the fulfilment of steady-state conditions in the accumulation are also studied. In many natural systems, metal speciation is dominated by the formation of complexes that can exhibit different lability degrees [24-27] i. e., metal availability is infuenced by the kinetics of the complex dissociation [28]. The last section is devoted to develop an interpretative framework to relate DGT concentrations with parameters of actual chemical species such as concentrations, diffusion coefficients and lability degrees.

2. Experimental Section

Solutions of Ni, Cd and Mg were prepared from the corresponding nitrate metal salts ($Ni(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich, $Cd(NO_3)_2 \cdot 4H_2O$, Merck and $Mg(NO_3)_2 \cdot 6H_2O$, Merck). Sodium nitrate, $NaNO_3$ (Sigma-Aldrich, puriss p.a.), was used as background electrolyte and MOPS (3-(N-morpholino)propanesulfonic acid), was used to buffer the solutions pH adjusted by dropwise addition of NaOH (Merck) or HNO_3 (Fluka). Triplicate standard DGT devices (piston type, 0.8 mm-thick diffusive disc, 0.4 mm-thick Chelex resin disc, and cellulose nitrate membrane filters (0.45 μm pore size, 0.125 mm-thick)) were used in the experiments. Metal accumulations were determined from their acid-eluted solutions via analysis with inductively coupled plasma mass spectrometry (ICP-MS, 7700 Series, Agilent) as described elsewhere [29].

Deployments in controlled fluctuating concentration solutions can be obtained in the lab by introducing the DGT devices in solutions of different concentrations during selected time periods. The total deployment time is, then, the addition of the times expended in each solution. For simplicity, we restrict ourselves in this work to the use of only two solutions, so that DGT devices undergo a pulse of concentration during the deployment. At the prescribed time, the DGT devices are extracted from the first solution and they are quickly introduced into the second one.

To cover different cases, we have studied i) accumulations under perfect sink conditions, like those of Ni, Cd and Mg (at low ionic strength), in solutions that are pulsed from 10^{-3} mol m^{-3} to 10^{-2} mol m^{-3} or viceversa at pH 6.5 (particular concentrations and pulse times are reported in Table 1); ii) accumulations of Mg at concentrations changing from 10^{-2} mol m^{-3} to 0.1 mol m^{-3} or viceversa and ionic strength above 10 mol m^{-3} which lead to non-negligible capacity effects (see also Table 1 for the detailed values and times) and iii) systems in presence of complexes. Nitrilotriacetic acid (NTA, Fluka, analytical grade) is known to form partially labile complexes with Ni when they are studied with DGT. The experimental runs consisted of deployments where the Ni concentration is pulsed to a higher or to a lower value at different times in a 8×10^{-2} mol m^{-3} solution of NTA buffered at pH = 7.50±0.01, T=25.0±0.1ºC and salt background 100 mol m^{-3} $NaNO_3$ as reported in Table 3. Additional experimental details are provided in the Supporting Information. Both, the accumulation regime and the presence of complexes can influence the relationship between c_{DGT} and the TWA concentration. This influence makes the study of these systems pertinent in this work.

3. Results and discussion

3.1 The standard DGT formulation

A main advantage of DGT lies in its design aiming at perfect-sink and steady-state conditions along a typical deployment in natural systems for measuring trace metal ions [8]. Under these conditions, the metal accumulation in the devices, n_M, can be written as

$$n_M = JAt = \frac{D_M c_{DGT}}{\delta^g} At \quad (1)$$

where D_M is the diffusion coefficient of the metal in the gel, δ^g is the thickness of the diffusive domain (diffusive gel + filter + diffusive boundary layer), *A* is the effective area of the device and *t* the deployment time. Notice that, for the sake of simplicity, eqn. (1) assumes a unique diffusion domain, although diffusion coefficients in water slightly differ from those in the gel. This is a good approximation for a thin diffusive boundary layer in comparison to a thick diffusive gel, as is the case in most well-stirred systems.

Eqn. (1) derives from a steady-state accumulation limited by diffusion of just one species at a fixed solution concentration. Accordingly, for the simplest case in which there is only metal at a constant concentration in the system, $c_{DGT} \approx c_M^*$ (the use of $\approx$ reminds us that there is a transient regime, not considered in Eqn. (1), and that perfect sink is a limiting behavior), where the superscript * indicates the bulk conditions. In presence of most background salts, there is some metal speciation. According to eqn. (11), in the section below devoted to systems with complexes, when all these metal species are fully labile and have diffusion coefficients similar to that of the hydrated metal, the total accumulation is the addition of the different contributions and Eqn. (1) can also be written as $c_{DGT} \approx c_{T,M}^*$ (where subscript “T” stands for “Total”). Systems with only metal and background salt are, thus, considered as made up with only one species, whose

concentration is $c^{*}_{T,M}$. The total metal concentration can, then, be estimated from the accumulation with the sole knowledge of the metal diffusion coefficient.

The steady-state regime generated from perfect-sink conditions is a limiting behaviour approached after an initial transient. For one species, the time to reach steady state, t_{ss}, can be estimated with the Einstein-Smoluchowski expression

$$t_{ss} \approx \frac{\left(\delta^{g}\right)^{2}}{2D_{M}} \quad (2)$$

which, for standard DGT values, indicates that t_{ss} for metals is of the order of 10 min. For more general systems, t_{ss} can be assessed by numerical simulation [30]. The fulfilment of perfect-sink conditions in simple metal solutions can be diagnosed from a negligible accumulation in the back resin disc (when a stack of two resin discs is used in the DGT device) or from the linearity in the plots accumulation vs. time, when the bulk metal concentration is constant, as prescribed by eqn. (1) [31, 32].

Obviously, most of the systems contain, in addition to the free hydrated ion, other metal species (typically metal complexes) that could exhibit either diffusion coefficients smaller than that of free metal, or slow dissociation rates. Consequently, the relative contribution of these species to the overall metal accumulation can be smaller compared to the free ion species, since they do not diffuse and/or dissociate fast enough. In these cases, c_{DGT}, operationally defined via Eqn. (1), can differ from the total or free metal concentration in the system. Actually, c_{DGT} is not a proper analytical concentration, but an operationally defined value, known as the DGT-labile concentration of the analyte in the solution, that can be interpreted as the hypothetical concentration of metal in a perfect-sink, ligand-free system that would yield the same accumulation as the real sample after the same deployment time [15, 33].

3.2 Systems with fluctuating concentrations: c_{DGT} as the TWA of the labile concentration along the deployment

Let us, now, derive a general property of c_{DGT} for systems with fluctuating concentrations. For the sake of simplicity, we restrict ourselves to systems with metal pulsed concentrations (i.e. bulk concentration constant during the pulse), since any concentration evolution can be reduced to this case by using short enough time intervals. Let c_{DGT_1} be the DGT-labile concentration of the system at the end of the isoconcentration interval (0, t_1) and let c_{DGT_2} be the value at the end of the interval (t_1, $t = t_1 + t_2$). Each value is experimentally accessible by introducing two sets of DGT devices at the beginning of the experiment and extracting one set at the end of each interval time. The difference in the average mass accumulated in both sets indicates the accumulation along the second time interval, which, together with the accumulation at the end of the first interval, can be converted into c_{DGT_1} or c_{DGT_2} by application of eqn. (1).

The total accumulation along the interval (0, t) can, then, be written as

$$n_M = \frac{D_M c_{DGT_1}}{\delta^g} A t_1 + \frac{D_M c_{DGT_2}}{\delta^g} A t_2 \quad (3)$$

and, applying Eqn. (1) to the total accumulation, c_{DGT} at time $t = t_1+t_2$, becomes

$$c_{DGT}(t) = c_{DGT_1} \frac{t_1}{t} + c_{DGT_2} \frac{t_2}{t} \quad (4)$$

which indicates that $c_{DGT}(t)$ at the end of the deployment is the time weighted average of the DGT-labile metal concentration in the system, which is expected to be of great interest in the correlation with toxicity effects. Extension of Eqn. (4) to multiple pulses is straightforward.

A main limitation of Eqn. (4) is that c_{DGT} is an effective or apparent concentration, so we might want to rewrite it in terms of real species. In order to bridge this gap, next sections will consider different fluctuating systems of increasing complexity and analyse the meaning of c_{DGT} in terms of real species, with special emphasis in its relationship with the time average metal concentration.

3.3 TWA concentration when only metal is present

3.3.1 Perfect sink conditions

Figure 1 depicts the experimental values of the total accumulation of Ni and Cd that were obtained with a pulsed bulk concentration ($c^*_{\mathrm{T,M_1}}$ up to t_1 and $c^*_{\mathrm{T,M_2}}$ from t_1 to $t = t_1 + t_2$) with the concentration values gathered in Table 1.

The time-averaged total metal concentration, $c^*_{\mathrm{T,M,Av}}$, can be defined as

$$c^*_{\mathrm{T,M,Av}} \equiv c^*_{\mathrm{T,M_1}} \frac{t_1}{t} + c^*_{\mathrm{T,M_2}} \frac{t_2}{t} \tag{5}$$

Piecewise linear accumulations of Ni and Cd are obtained when the metal concentration is constant, suggesting that the accumulation of these metals follows perfect-sink conditions (with negligible transient). As only these metal cations are present in the system, c_{DGT_i} is then equal to $c^*_{\mathrm{T,M}_i}$ and eqn. (4) implies

$$c_{\mathrm{DGT}}(t) = c^*_{\mathrm{T,M,Av}} \tag{6}$$

Eqn. (6) is a particular case of Eqn. (4) indicating that, in solutions of only metals, c_{DGT} coincides with the experimental time average of the total metal concentration whenever the accumulation takes place under perfect-sink conditions with negligible transient effects, as seen in Table 1 for Cd and Ni accumulations. The non-linearity of this

accumulation *vs*. time curve reflects, then, a fluctuating bulk concentration. However, downward-bent accumulations also arise when equilibrium or capacity effects are non-negligible. These two cases can be recognized using DGT devices with two resin discs. A negligible metal accumulation in the bottom resin disc points towards a fluctuating concentration under perfect sink conditions, while capacity effects lead to non- negligible accumulations in the bottom resin disc.

3.3.2 Transient effects

Anthropogenic or natural variations, like temperature changes from night to day or tides in estuaries, induce fluctuations in the metal concentrations in natural systems. In the section above, transient effects in the DGT accumulation have been neglected and instantaneous attainment of perfect-sink conditions was assumed. This is a good approximation for a long enough time span (t >>10 min, according to the Einstein-Smoluchowski estimation given by (2)). However, we may ask ourselves about the impact of the transient on the difference between c_{DGT} and the TWA in the case of short fluctuations.

Both, a suitable analytical expression [34] or numerical simulations, can be used to assess c_{DGT} as a surrogate of the TWA when the transient period is non-negligible. Numerical simulation is used here to compute the theoretical accumulation under transient conditions and eqn. (1) is used to compute the corresponding c_{DGT}. Results are reported in Fig. 2 and Table 2. At the beginning of the experiment and when the concentration jumps towards higher values at t = 2h (see Fig. 2), c_{DGT} underestimates $c^*_{T,M,Av}$ since the transient accumulation rate is smaller than the steady-state one. This is also reflected in Fig. 2 by the relative difference, defined as

$$E = \frac{c^*_{T,M,Av} - c_{DGT}}{c^*_{T,M,Av}} \quad (7)$$

which shows two peaks: at the starting time and after the concentration jump. After 30 minutes of deployment, *E* still amounts to 19%, but it falls to 5% at $t = 2$ h. This decrease in the difference (when the duration of the transient regime becomes progressively negligible in front of the pulse length) implies negligible differences between c_{DGT} and the TWA concentration for fluctuations with pulses of 12 h duration as in many natural phenomena.

When the concentration jumps towards a smaller value, the effect of the transient is opposite, since the accumulation rate along the transient is higher than the steady-state one, and thus c_{DGT} tends to overestimate $c^*_{T,M,Av}$. Transients towards higher or towards lower concentrations have, then, opposite effects on the difference between c_{DGT} and $c^*_{T,M,Av}$ and tend to cancel out in a series of alternating pulses at two bulk concentrations. It seems, then, convenient to examine the agreement of c_{DGT} with the TWA when periodic pulses of concentration of different frequencies take place.

Table 2 gathers the relative difference *E* due to a 10-fold concentration jump for pulse durations in the range of 10 to 40 min. Notice that, as the pulse time increases (we move from left to the right along a row of Table 2), the difference decreases, since the accumulation proceeds mostly under steady state and transient becomes negligible. Going down in a column, the relative difference is not monotonous. When the concentration increases, *E* increases, but when the concentration jumps to a smaller value, there is an opposite effect and *E* is considerably reduced. Additionally, the mass accumulated in previous pulses tends to progressively reduce the relative influence of each new transient, so that going down along a column, the relative differences tend to decrease. Calculations for other concentration jumps are included in Table S3, but differences with values

reported in Table 2 are small. This Table also suggests that, to use c_{DGT} as an estimate of the TWA concentration, the duration of the pulses is more important than the size of the jump. It is worth mentioning here that square pulses maximize transient effects in comparison to more smoothed variations.

3.3.3 Equilibrium effects

As previously reported [32], the accumulations of Mg proceed under perfect-sink conditions at low ionic strength, $I < 10$ mol m^{-3} (see also Fig. S1 in the SI). The linearity of Mg accumulation seen in Fig. 3A during both time intervals of fixed bulk concentration confirms the fulfilment of these conditions. Accordingly, Eqn. (1) can be used to calculate the TWA Mg concentration at $I = 10$ mol m^{-3} at the end of the first pulse or at the end of the corresponding experiment. Good agreement between c_{DGT} and $c^*_{T,M,Av}$ both, at t_1 and at $t = t_1+t_2$, can be seen in Table 1 ($c^*_{T,M,Av}$ at t_1 is c^*_{T,M_1}).

Conversely, due to the decrease of the equilibrium constant of the Mg binding to the Chelex beads when the ionic strength increases, effective-capacity effects lead to non-linear accumulations for Mg at values of I higher than 10 mol m^{-3} (see the accumulation curve corresponding to $I = 500$ mol m^{-3} in Fig. 3B), together with reported non-negligible back accumulation in a DGT with two resin discs [32]. So, Mg is helpful to exemplify equilibrium effects on the relationship between c_{DGT} and $c^*_{T,M,Av}$. As reported in Table 1, Eqn (1) yields $c_{DGT}(t_1) = 1.87\times10^{-2}$ mol m^{-3} and $c_{DGT}(t = t_1+t_2) = 2.96\times10^{-3}$ mol m^{-3} for the data of Fig. 3B in disagreement respectively with the experimental $c^*_{Mg_1} = 9.57\times10^{-2}$ mol m^{-3} along the deployment in the first solution or the average concentration, $c^*_{T,M,Av} = 5.35\times10^{-2}$ mol m^{-3}, for the whole experiment. These results indicate that DGT

cannot provide accurate TWA concentrations of Mg under these experimental conditions. Actually, in the limiting case when the metal bound reaches equilibrium with its solution concentration, the history of the accumulation is absolutely lost, since this equilibrium is only dependent on the current solution concentration and fully independent from the concentration variation during the accumulation. Non-linear accumulations have also been reported in other cases dealing with metals [29, 35] or organic contaminants [13, 36].

3.4 Influence of complexes on the TWA determination

3.4.1 Relationships in the presence of complexes

Natural systems contain large mixtures of ligands. In the simplest case of a 1:1 stoichiometric relationship, a set of parallel reactions involving *h* ligands (denoted from ^{1}L to ^{h}L) lead to the formation of *h* complexes, denoted M^{j}L,

$$\mathrm{M} + {}^{j}\mathrm{L} \underset{k_{\mathrm{d},j}}{\overset{k_{\mathrm{a},j}}{\rightleftharpoons}} \mathrm{M}\,{}^{j}\mathrm{L} \qquad j = 1..\,h \tag{8}$$

It can be shown that, when c_{M} vanishes at the resin-diffusive gel interface $x = \delta^{r}$, i.e., perfect-sink conditions apply for the metal, the total flux, assuming steady state and time-independent bulk concentrations, can be formally written as [37]

$$J = \frac{D_{\mathrm{M}} c^{*}_{\mathrm{M}}}{\delta^{\mathrm{g}}} + \sum_{j=1}^{h}\left[\frac{D_{\mathrm{M}^{j}\mathrm{L}}\, c^{*}_{\mathrm{M}^{j}\mathrm{L}}}{\delta^{\mathrm{g}}}\,\xi_{j}\right] \tag{9}$$

where index *j* scans all the complexes in the system with the individual lability degree ξ_j of the complex M^{j}L defined as

$$\xi_{j} \equiv 1 - \frac{c^{r}_{\mathrm{M}^{j}\mathrm{L}}}{c^{*}_{\mathrm{M}^{j}\mathrm{L}}} \tag{10}$$

where $c^{r}_{\mathrm{M}^{j}\mathrm{L}}$ denotes the complex concentration at the resin-diffusive gel interface. Previous Eqns. (9) and (10) hold even in the absence of ligand excess [37].

The meaning of Eqn. (9) is quite simple: the total flux is just the sum of the free metal flux plus a fraction, ξ_j, of the maximum possible contribution of each complex ($\frac{D_{\mathrm{M}^{j}\mathrm{L}} c^{*}_{\mathrm{M}^{j}\mathrm{L}}}{\delta^{\mathrm{g}}}$). ξ_j ranges between 0 (totally inert complex) and 1 (fully labile complex).

If *J* given by eqn. (9) is used in eqn. (1), c_{DGT} becomes

$$c_{\mathrm{DGT}}(t) = c^{*}_{\mathrm{M}} + \sum_{j=1}^{h} \frac{D_{\mathrm{M}^{j}\mathrm{L}}}{D_{\mathrm{M}}} \xi_j c^{*}_{\mathrm{M}^{j}\mathrm{L}} \tag{11}$$

which states that c_{DGT} is the addition of the free metal concentration and the labile fraction of each complex, $\xi_j c^{*}_{\mathrm{M}^{j}\mathrm{L}}$, modulated by a diffusional factor $\frac{D_{\mathrm{M}^{j}\mathrm{L}}}{D_{\mathrm{M}}}$ [15, 33, 38].

The above formulation can be used to write the total accumulation in a solution with free metal concentration $c^{*}_{\mathrm{M}_1}$ until time t_1 and $c^{*}_{\mathrm{M}_2}$ from t_1 until time $t = t_1 + t_2$, as the addition of the accumulations at the specific time intervals, $n_{\mathrm{M}} = J_1 A t_1 + J_2 A t_2$.

By using Eqn. (9) and Eqn. (1) to obtain $c_{\mathrm{DGT}}(t)$ at the end of the deployment, $c_{\mathrm{DGT}}(t)$ can be written in terms of the concentrations of the real species present in the system as

$$c_{\mathrm{DGT}}(t) = \frac{c^{*}_{\mathrm{M}_1} t_1 + c^{*}_{\mathrm{M}_2} t_2}{t} + \sum_{j=1}^{h} \frac{D_{\mathrm{M}^{j}\mathrm{L}}}{D_{\mathrm{M}}} \left(\frac{\xi_{j,1} c^{*}_{\mathrm{M}^{j}\mathrm{L}_1} t_1 + \xi_{j,2} c^{*}_{\mathrm{M}^{j}\mathrm{L}_2} t_2}{t} \right) \tag{12}$$

where $\xi_{j,i}$ stands for the lability degree of M^{j}L under the bulk concentrations of the time interval *i*. Expression (12) clearly indicates that $c_{\mathrm{DGT}}(t)$ depends on the speciation, the mobility and the lability degree of the complexes at each time interval. Both, the speciation and the lability degree can vary due to the jump of concentration, temperature,

pH, ionic strength, or any other fluctuating physicochemical factor. Extension of Eqn. (12) to multiple pulses is straightforward.

The presence of partially labile complexes is suggested by a non-negligible accumulation in the back resin disc when a stack of two resin discs is used in the DGT device [39, 40]. Since $\xi \le 1$ and usually $D_{\mathrm{M}^j\mathrm{L}} < D_{\mathrm{M}}$, eqn. (12) indicates that $c_{\mathrm{DGT}}(t)$ underestimates the TWA total metal concentration whenever complexes with lower diffusivity than the free metal or partially labile complexes are present in the solution. This can explain why in many cases [18, 41-43] $c_{\mathrm{DGT}}(t)$ tends to underestimate the average of grab sampling measurements.

If all diffusion coefficients are similar ($D_{\mathrm{M}} \approx D_{\mathrm{M}^j\mathrm{L}} \quad \forall j$)

$$c_{\mathrm{DGT}}(t) = \frac{\left(c^*_{\mathrm{M}_1} + \sum_{j=1}^{h} \xi_{j,1} c^*_{\mathrm{M}^j\mathrm{L}_1}\right) t_1 + \left(c^*_{\mathrm{M}_2} + \sum_{j=1}^{h} \xi_{j,2} c^*_{\mathrm{M}^j\mathrm{L}_2}\right) t_2}{t} \tag{13}$$

which indicates that $c_{\mathrm{DGT}}(t)$ is the TWA of the total labile metal concentration at each time interval.

ξ_j in the mixture are not directly measurable, but they can be approximated with the values of the lability degree in single ligand systems [44], thus reducing the number of unknowns in (13). More interestingly, for strong complexes and excess of ligand conditions, the free metal is negligible and the lability degree of a complex, ξ_j, could be independent of the time interval, since the lability of complexes in DGT shows a mild dependence on the ligand concentration under excess of ligand [27, 37, 44]. Then, eqn. (12) becomes

$$c_{\mathrm{DGT}}(t) = \frac{\left(\sum_{j=1}^{h} \frac{D_{\mathrm{M}^j\mathrm{L}}}{D_{\mathrm{M}}} \xi_j \left(c^*_{\mathrm{M}^j\mathrm{L}_1} t_1 + c^*_{\mathrm{M}^j\mathrm{L}_2} t_2\right)\right)}{t} \tag{14}$$

which, for only one complex reduces to

$$c_{\mathrm{DGT}}(t)=\frac{D_{\mathrm{ML}}}{D_{\mathrm{M}}}\xi\left(\frac{c^{*}_{\mathrm{ML}_1}t_1+c^{*}_{\mathrm{ML}_2}t_2}{t}\right)=\frac{D_{\mathrm{ML}}}{D_{\mathrm{M}}}\xi c^{*}_{\mathrm{T,M,Av}} \quad (15)$$

indicating that $c_{\mathrm{DGT}}(t)$ is the product of the TWA metal concentration during the deployment, the lability degree and the ratio of the diffusion coefficient of the complex with respect to that of the free metal.

If the complex is fully labile and has a common diffusion coefficient with the free metal, $c_{\mathrm{DGT}}(t)$ estimates directly $c^{*}_{\mathrm{T,M,Av}}$ during the deployment. Otherwise $c_{\mathrm{DGT}}(t)$ underestimates the time average total metal concentration in the system, but –as will be shown below- an estimation of the TWA metal concentration can be obtained by correcting $c_{\mathrm{DGT}}(t)$ taking into account the relationship (15).

3.4.2 The TWA Ni concentration in presence of an excess of NTA

Ni accumulations in solutions with different Ni to NTA concentration ratios are reported in Table 3, which also details the particular conditions of each deployment together with the time average concentrations and the measured c_{DGT} values at the end of the deployment. Experimental accumulations are plotted in Fig. 4. As seen in Table 3, c_{DGT} clearly underestimates $c^{*}_{\mathrm{T,M,Av}}$, indicating that c_{DGT} cannot be seen as a direct estimator of the time weighted concentration. Let us try to explain these results and how to find the TWA using the theoretical framework developed above.

Ni reacts with NTA according to

$$\mathrm{Ni^{2+}}+\mathrm{NTA^{3-}}\rightleftharpoons\mathrm{NiNTA^{-}} \quad (16)$$

Equilibrium speciation as predicted with the speciation code VMinteq (Table S1) indicates that $\mathrm{Ni(NTA)_2^{4-}}$ and free Ni concentrations are negligible in the conditions of the experiments.

The use of the general expression (12) to interpret c_{DGT} in terms of concentrations of real species requires the knowledge of the lability degrees of NiNTA in both solutions. These values have been measured from the accumulation in dedicated experiments reported in Figs. 5A and B. Recalling that the free Ni concentration is negligible, Eqn. (9) becomes

$$\xi \approx \frac{n_{Ni}/At}{D_{NiNTA}\frac{c^*_{NiNTA}}{\delta^g}} \quad (17)$$

where n_{Ni} stands for the number of accumulated Ni moles. The slope of the regression line, n_{Ni}/t equals 5.1931 (Fig 5A) or 0.9745 (Fig 5B) in the respective solutions. Using A=3.14×10^{-4} m^2, D_{NiNTA}=5.53×10^{-10} m^2/s, δ^g=1.13×10^{-3} m and the values reported in Table S1, one finds $\xi \approx$ 0.431 and 0.430 for the low and high concentration cases, respectively. This indicates that, as expected [27, 37, 44], there is a negligible change of the lability degree due to the change of the Ni concentration, since NTA excess prevails. So, eqn. (15) can be expressed as

$$c^*_{T,M,Av} = c_{DGT}(t)\frac{D_M}{D_{ML}}\frac{1}{\xi} \quad (18)$$

Values of $c_{DGT}(t)\frac{D_M}{D_{ML}}\frac{1}{\xi}$ have been included in Table 3, showing good agreement with $c^*_{T,M,Av}$. This agreement holds for deployments in which the concentration of Ni jumps up or down during the deployment. Equation (18) is, then, a simple way to correct c_{DGT} when we are interested in TWA metal concentrations in presence of a dominant complex. The

values of $\frac{D_M}{D_{ML}} = 1.08$ and ξ=0.43 render $\frac{D_M}{D_{ML}}\frac{1}{\xi} = 2.51$ justifying why c_{DGT} underestimates $c^*_{T,M,Av}$ in the present system.

For experiments 14-16 in Table 3, there is a high amount of Ni accumulated in the resin at the end of the deployment in the concentrated solution, so that when the Ni concentration in the solution drops by a factor of 5, the accumulation does not increase as can be seen in panel C of Fig. 4. This behaviour suggests that the Ni accumulation in the first time interval reaches or exceeds the equilibrium value of the Ni accumulation for the second solution, so that equilibrium effects, analogous to those shown in section 3.3.3, arise. The difference between $c^*_{T,M,Av}$ and $c_{DGT}(t)\frac{D_M}{D_{ML}}\frac{1}{\xi}$ is still small in Table 3, due to the low Ni concentration along the (relatively) short deployment in the second solution, i. e., the accumulation in the high Ni solution is so long and relevant that the accumulation in the second solution is, in comparison, almost negligible. When the deployment time in the concentrated Ni solution decreases, see experiments 11-13 in Table 3, equilibrium effects disappear, the accumulation in the low Ni concentration solution follows the expected trend, see panel B in Fig. 4, and $c_{DGT}(t)\frac{D_M}{D_{ML}}\frac{1}{\xi}$ becomes a good estimator of $c^*_{T,M,Av}$.

4. Conclusions

In systems with fluctuating concentrations, c_{DGT} can be seen as the time-weighted average of the DGT-labile concentration along the deployment. In simple metal solutions, c_{DGT} approaches the time average of the total metal concentration (see eqn.(4)), provided that the accumulation takes place under perfect sink and steady-state conditions. These conditions require a negligible back accumulation when a stack of two resin discs in a

DGT device is used. Due to transient effects becoming progressively significant, differences between c_{DGT} and $c^*_{T,M,Av}$ increase with decreasing pulse duration (see table 2). In presence of complexes, as seen in eqn. (12), c_{DGT} underestimates $c^*_{T,M,Av}$ whenever these complexes are partially labile or less mobile than the free metal. The presence of partially labile complexes can be assessed by a non-negligible back accumulation if a stack of two resin discs is used in the DGT device. When a complex is dominant, eqn. (18) provides a simple correction factor to improve the estimation of $c^*_{T,M,Av}$ from c_{DGT}.

Supporting Information

A Supporting Information file reports details of the experimental procedure, test solutions and parameters used, additional data on the influence of the transient regime in the estimation of the TWA concentration, and additional data of the Mg accumulation at different ionic strengths.

Acknowledgments

The authors gratefully acknowledge support for this research from the Spanish Ministry MCIU/AEI (Project CTM2016-78798) and FEDER UE

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Figures

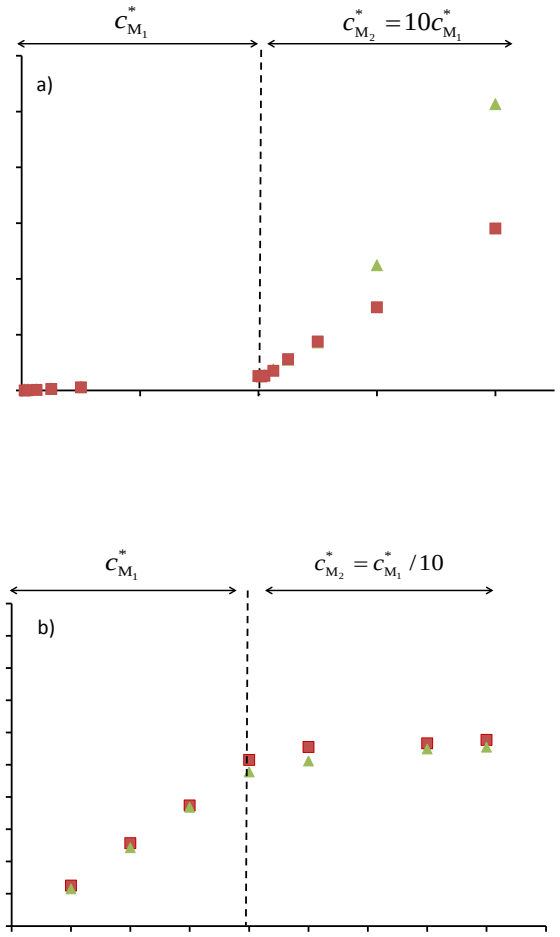

Figure 1. Time evolution of the total accumulation of Ni (green triangles) and Cd (red squares) in an experiment with a) a pulsed increase of the bulk solution concentration and b) a pulsed decrease of the bulk solution concentration at 4h. Experimental conditions are detailed in Table 1. The vertical dashed line (at t_1) separate different bulk solutions.

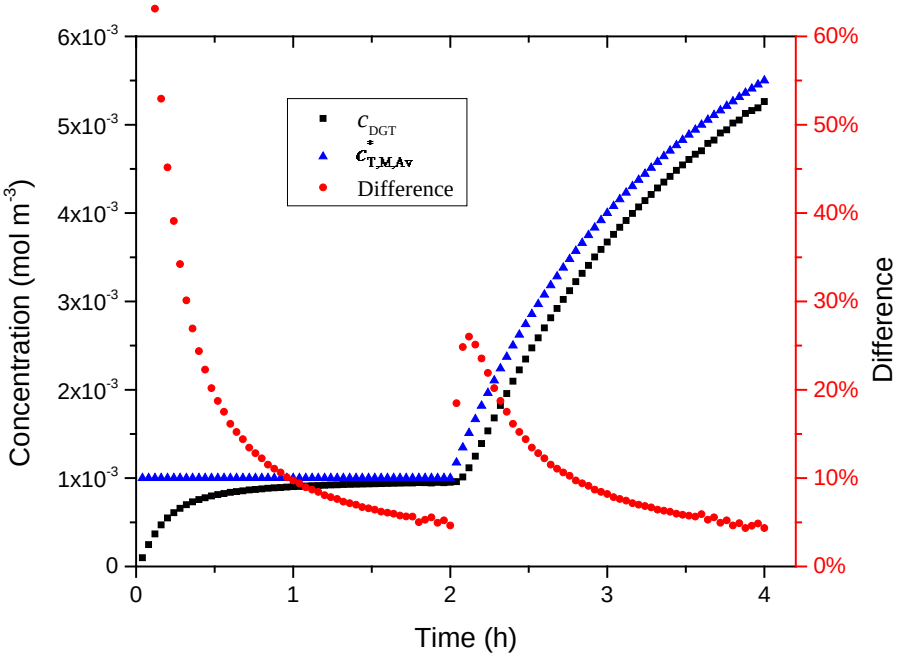

Figure 2 Time evolution of $c_{DGT}(t)$ *(black squares, left ordinate axis), the time-averaged total metal concentration,* $c^{*}_{T,M,Av}$ *(blue triangles, left ordinate axis), and their relative error or difference E, see eqn(7),* $E = \left(\frac{c^{*}_{T,M,Av} - c_{DGT}}{c^{*}_{T,M,Av}} \right)$ *(red circles, right ordinate axis), in an experiment with a pulsed bulk Cd concentration at 2 h.* $c_{DGT}(t)$ *values are obtained by numerical simulation of the Cd accumulation. Concentrations:* c^{*}_{T,M_1} *=1×10-3 mol m-3 for 0<t<2h and* c^{*}_{T,M_2} *=1×10-2 mol m-3 for 2<t<4h. Other parameters: association and dissociation kinetic constants of Cd with Chelex beads* $k_{a,R}$ *= 10⁶ m³ mol-1 s-1,* $k_{d,R}$ *= 10-2 s-1 and* D_{Cd} *= 6.30×10-10 m² s-1.*

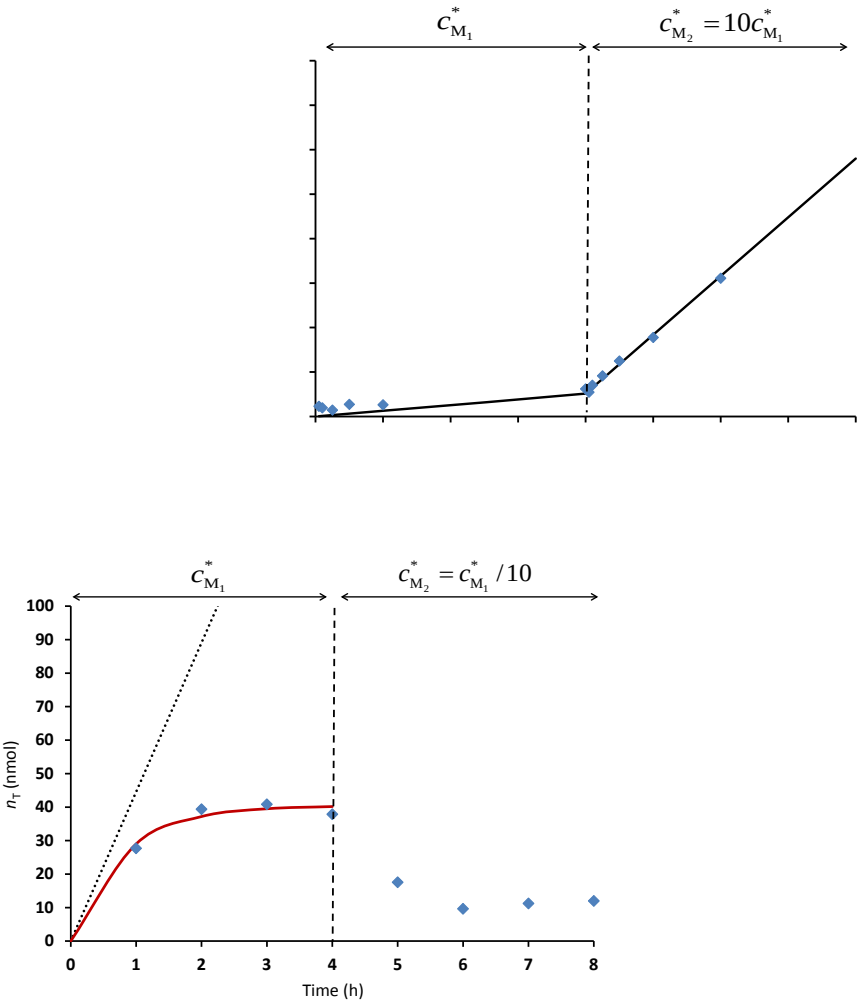

Figure 3. Time evolution of the total accumulation of Mg (blue diamonds) along an experiment with a change in solution concentration at 4 h. a): Ionic strength 10 mol m^{-3}. Continuous line stands for perfect-sink accumulations. b): Ionic strength 500 mol m^{-3}. Continuous line corresponds to Eqn. (5) in reference [45]. Dotted line stands for the expected perfect-sink accumulation. Parameters: D_{Mg} = 4.94×10^{-10} m^2 s^{-1}. Experimental conditions as indicated in Table 1. The vertical dashed line (at t_1) separate different bulk solutions.

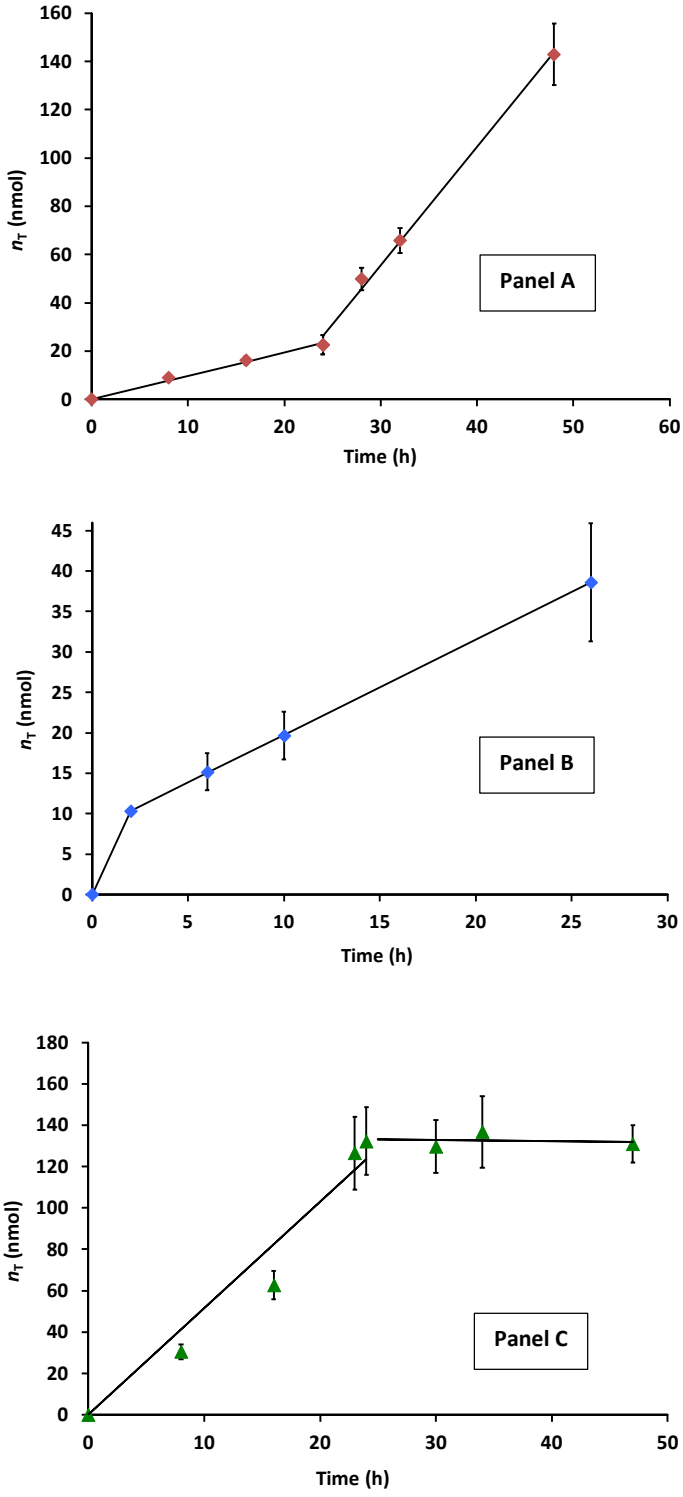

Figure 4. Time evolution of Ni accumulation in NiNTA solutions. a): Deployment with an increase in the bulk concentration of Ni at 24 hours; b): deployment with a decrease in the bulk Ni concentration at 2 hours. C: deployment with a decrease in the bulk concentration at 24 hours. Experimental conditions as indicated in Table 3. Continuous line stands for the linear regression of the accumulations vs. time in the interval.

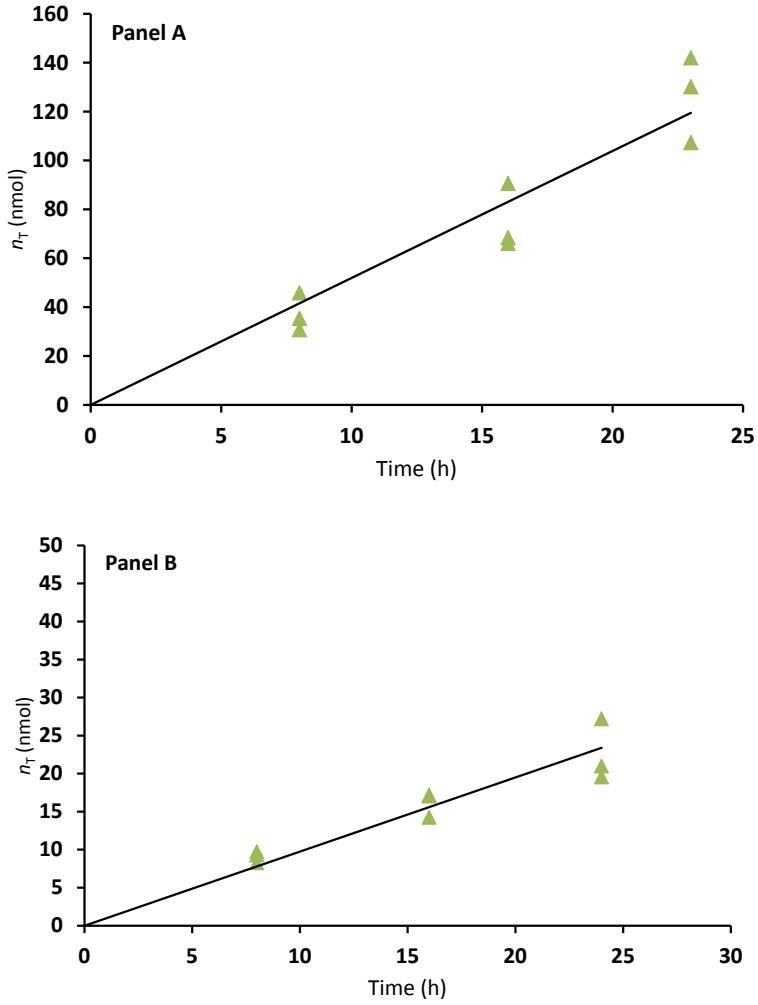

Figure 5. Time evolution of Ni accumulation in a Ni+NTA solution. a): $c^*_{T,Ni}$ *=2.15×10^{-2} mol m^{-3}; b):* $c^*_{T,Ni}$ *=4.19×10^{-3} mol m^{-3}. Continuous line stands for the linear regression of accumulations vs. time with intercept equal to zero. Other parameters:* $c^*_{T,NTA}$ *=8×10^{-2} mol m^{-3}, pH = 7.50 ± 0.01, T = 25.0 ± 0.1 ºC and salt background 100 mol m^{-3}*

Tables

Table 1. Metal concentrations and deployment times in solutions that contain only Cd, Ni or Mg in background salt. Other experimental conditions: pH = 6.50 ± 0.01 and T = 25.0 ± 0.1 ºC. Last three columns stand for the average total metal concentration during the deployment, $c^*_{T,M,Av}$, $c_{DGT}(t_1)$ *calculated at the end of the deployment in the first solution and* $c_{DGT}(t_1+t_2)$ *calculated at the end of the experiment.*

		t_1 (h)	c^*_{T,M_1} (mol m^{-3})	t_2 (h)	c^*_{T,M_2} (mol m^{-3})	$c^*_{T,M,Av}$ (mol m^{-3})	$c_{DGT}(t_1)$ (mol m^{-3})	$c_{DGT}(t_1+t_2)$ (mol m^{-3})
Cd^{2+}	**Exp. 1 (*I* = 10 mol m^{-3})**	4	1.19×10^{-3}	2	1.21×10^{-2}	3.37×10^{-3}	1.00×10^{-3}	2.71×10^{-3}
	Exp. 2 (*I* = 500 mol m^{-3})	4	9.42×10^{-3}	4	0.95×10^{-3}	5.18×10^{-3}	9.95×10^{-3}	5.57×10^{-3}
Ni^{2+}	**Exp. 1 (*I* = 10 mol m^{-3})**	4	1.15×10^{-3}	2	1.18×10^{-2}	4.70×10^{-3}	1.02×10^{-3}	5.79×10^{-3}
	Exp. 2 (*I* = 500 mol m^{-3})	4	8.79×10^{-3}	4	0.90×10^{-3}	4.85×10^{-3}	9.58×10^{-3}	5.56×10^{-3}
Mg^{2+}	**Exp. 1 (*I* = 10 mol m^{-3})**	4	1.15×10^{-2}	2	1.17×10^{-1}	4.67×10^{-2}	1.14×10^{-2}	4.66×10^{-2}
	Exp. 2 (*I* = 500 mol m^{-3})	4	9.57×10^{-2}	4	1.12×10^{-2}	5.35×10^{-2}	1.87×10^{-2}	2.96×10^{-3}

Table 2. Theoretical relative difference, E (defined in eqn. (7) as a percentage) between c_{DGT} *and* $c^*_{T,M,Av}$ *when the concentration of just one metal ion jumps repetitively between* c^*_{T,M_1} *=10^{-3} and* c^*_{T,M_2} *=10^{-2} mol m^{-3} for different pulse times (t_p =10, 20, 30 and 40 minutes). Exposure concentration in the first row is* c^*_{T,M_1} *and jumps when time goes from one row to the next one, so that it follows a square wave between the values* c^*_{T,M_1} *and* c^*_{T,M_2}*. The measurement takes place at the end of each pulse. Parameters for the calculation of* c_{DGT}*: D_M = 6.08×10^{-10} m^2 s^{-1}; δ=1.13×10^{-3} m; A=3.14×10^{-4} m^2.*

		Pulse time (t_p)

Measurement time	$C^{*}_{T,M,Av}$ (mol m^{-3})	10 min		20 min		30 min		40 min	
		C_{DGT} (mol m^{-3})	E	C_{DGT} (mol m^{-3})	E	C_{DGT} (mol m^{-3})	E	C_{DGT} (mol m^{-3})	E
t_p	1.00×10^{-3}	4.67×10^{-4}	53%	7.10×10^{-4}	29%	8.06×10^{-4}	19%	8.53×10^{-4}	15%
2 t_p	5.50×10^{-3}	2.78×10^{-3}	49%	4.04×10^{-3}	26%	4.52×10^{-3}	18%	4.77×10^{-3}	13%
3 t_p	4.00×10^{-3}	3.68×10^{-3}	8%	3.90×10^{-3}	3%	3.92×10^{-3}	2%	3.95×10^{-3}	1%
4 t_p	5.50×10^{-3}	4.14×10^{-3}	25%	4.76×10^{-3}	13%	5.01×10^{-3}	9%	5.13×10^{-3}	7%
5 t_p	4.60×10^{-3}	4.42×10^{-3}	4%	4.53×10^{-3}	2%	4.55×10^{-3}	1%	4.56×10^{-3}	1%
6 t_p	5.50×10^{-3}	4.59×10^{-3}	17%	5.01×10^{-3}	9%	5.17×10^{-3}	6%	5.26×10^{-3}	4%

Table 3. Total Ni concentrations and deployment times in solutions that contain Ni and NTA; average total metal concentrations during the deployment, $c^*_{T,M,Av}$*;* c_{DGT} *calculated at the end of the deployment and the products* $c_{DGT}\frac{D_M}{D_{ML}}\frac{1}{\xi}$*. Parameters:* $c^*_{T,NTA}$ *= 8·10-2 mol m-3, A=3.14×10-4 m2,* D_{NiNTA}*=5.53×10-10 m2 s-1,* $\frac{D_M}{D_{ML}}=1.08$*,* δ^g *=1.13×10-3 m,* c^*_{MOPS} *= 1 mol m-3, pH = 7.50 ± 0.01, T = 25.0 ± 0.1 ºC and salt background 100 mol m-3.*

	t_1 (h)	c^*_{T,Ni_1} (mol m^{-3})	t_2 (h)	c^*_{T,Ni_2} (mol m^{-3})	$c^*_{T,M,Av}$ (mol m^{-3})	c_{DGT} (mol m^{-3})	$c_{DGT}\frac{D_M}{D_{ML}}\frac{1}{\xi}$ (mol m^{-3})
Exp. 1	8	2.15×10^{-2}	0	4.19×10^{-3}	2.15×10^{-2}	8.99×10^{-3}	2.23×10^{-2}
Exp. 2	16	2.15×10^{-2}	0	4.19×10^{-3}	2.15×10^{-2}	8.99×10^{-3}	2.23×10^{-2}
Exp. 3	23	2.15×10^{-2}	0	4.19×10^{-3}	2.15×10^{-2}	8.99×10^{-3}	2.23×10^{-2}
Exp. 4	24	2.15×10^{-2}	0	4.19×10^{-3}	2.15×10^{-2}	8.99×10^{-3}	2.23×10^{-2}
Exp. 5	0	2.15×10^{-2}	8	4.19×10^{-3}	4.19×10^{-3}	1.69×10^{-3}	4.19×10^{-3}
Exp. 6	0	2.15×10^{-2}	16	4.19×10^{-3}	4.19×10^{-3}	1.69×10^{-3}	4.19×10^{-3}
Exp. 7	0	2.15×10^{-2}	24	4.19×10^{-3}	4.19×10^{-3}	1.69×10^{-3}	4.19×10^{-3}
Exp. 8	24	4.40×10^{-3}	4	2.34×10^{-2}	7.11×10^{-3}	3.01×10^{-3}	7.47×10^{-3}
Exp. 9	24	4.40×10^{-3}	8	2.34×10^{-2}	9.14×10^{-3}	3.65×10^{-3}	9.06×10^{-3}
Exp. 10	24	4.40×10^{-3}	24	2.34×10^{-2}	1.39×10^{-2}	5.14×10^{-3}	1.28×10^{-2}
Exp. 11	2	2.34×10^{-2}	4	4.40×10^{-3}	1.07×10^{-2}	4.46×10^{-3}	1.11×10^{-2}
Exp. 12	2	2.34×10^{-2}	8	4.40×10^{-3}	8.19×10^{-3}	3.34×10^{-3}	8.28×10^{-3}
Exp. 13	2	2.34×10^{-2}	24	4.40×10^{-3}	5.86×10^{-3}	2.30×10^{-3}	5.71×10^{-3}
Exp. 14	24	2.15×10^{-2}	6	4.19×10^{-3}	1.80×10^{-2}	7.53×10^{-3}	1.87×10^{-2}
Exp. 15	24	2.15×10^{-2}	10	4.19×10^{-3}	1.64×10^{-2}	6.84×10^{-3}	1.70×10^{-2}
Exp. 16	24	2.15×10^{-2}	23	4.19×10^{-3}	1.30×10^{-2}	5.42×10^{-3}	1.35×10^{-2}